Creation of an Optimal Annealing Schedule for Self-Assembly

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Abstract

The goal of the research was to develop a temperature versus time schedule to make the process of self-assembly occur in an optimal manner. Self-assembly is any process in which a system becomes more ordered without pervasive outside interference.

In order to create a temperature versus time schedule, or annealing schedule, a particular system needed to be considered. The system used was reported by Grzybowski et al. [1]. The system is at the macroscopic level and consisted of spheres of equal and opposite charge. When perturbed the system would form a square lattice in two dimensions.

This system was the model system used for the project of optimizing self-assembly. It was chosen for its relative simplicity and ease in modeling. In order to make the model more computationally tractable simplifications were made to the system.

An assumption about the rate of self-assembly was made and justified. This assumption along with system information produced the optimal schedule when classical control theory was applied. The schedule created outperformed other common annealing schedules.

Background

Introduction and Motivation:

Self-assembly is a widespread phenomenon with many systems exhibiting the behavior [2], some examples include colloids [3], suspensions [4] and biological systems[5]. Because such behavior is being considered for use in lithography [6,7] and the production of microelectronic devices [8] optimizing the behavior becomes commercially important. For many systems the better ordered a material is the properties which make that material valuable become enhanced. From a manufacturing perspective an optimal annealing schedule is useful to make a higher quality product due to enhanced assembly in addition to a reduction in production time. A simple example of this is tempering metal, a better annealing schedule could help strengthen a metal and do so in a shorter amount of time. The work done in this project outlines a way to produce a schedule for a particular system, however it is presumable that the techniques and assumptions made will be applicable to other systems of commercial or scientific interest.

System Background:

A simple system was needed to explore the goal of optimizing self-assembly. The system chosen was one experimentally explored by Grzybowski et al. [ref], pictured below. Physically the system consists of two types of spherical beads with equal and opposite charge approximately 3 millimeters in diameter. The two materials used depended on the experiment, the materials that created the square lattice were polymethylmethacrylate or PMMA and Teflon. The reason those two materials produced a square lattice is that the charge produced between the two were of equal and opposite

charge. Other materials were used to create different charge ratios and thus different kinds of lattices, for example a 2 to 1 charge ratio created a hexagonal lattice system. For all materials the charges were induced by contact charge transfer as the beads rolled on the surface of a tray which was coated in gold. Because of the different physical properties of the two materials the beads became charged with opposite charges very close in magnitude.

The system alone does a poor job in forming a square lattice. This is because the system will relax to its local energy minimum and remain there. To avoid the system getting stuck in these meta-stable states the tray containing the beads oscillated in the plane of the tray. This shaking would impart kinetic energy onto the beads through surface friction or boundary collisions allowing the system to escape a local minimum. The computational model created for this project used a thermostat to impart kinetic energy to the system. Experimentally the methods used to get the system to assemble where heuristic and adjusted in real time by the experimenter based on the behavior of the system.

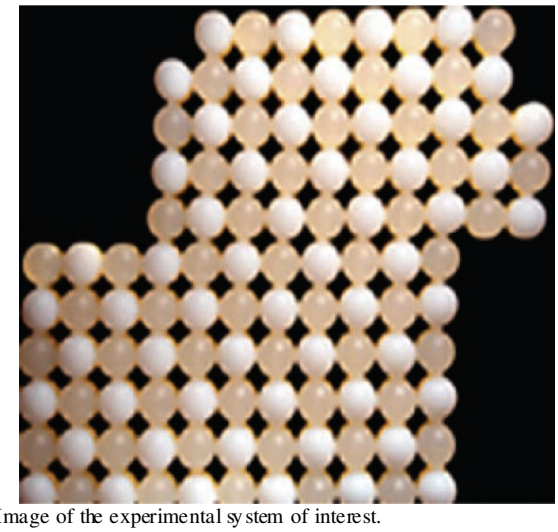

Image of the experimental system of interest.
Grzybowski B.A., Winkleman A., Wiles J.A., Brumer Y. and Whitesides G. M., *Nature Materials,* **2003**, 2, 241-245.

Previous Work:

Previous work has been done in the computational field to find an optimal simulated annealing schedule. A simulated annealing schedule is a temperature schedule used in Monte-Carlo sampling and not direct dynamics. Simulating annealing is more computationally tractable and thus more attractive for earlier computers. This earlier work approached the problem by creating a schedule that produced the minimum entropy path as the system annealed (reference). The resulting schedule is known as the Constant Thermodynamic Speed Model and the equations that came from this work are:

$$\frac{dT}{dt} = -\frac{\nu T}{\varepsilon\sqrt{C}} \qquad \text{(eq. 1)}$$

with T = temperature, t = time, C = the heat capacity, ε = relaxation time, ‹E› = system mean energy, σ = the standard deviation of the systems natural fluctuations, E_{eq} = the equilibrium system energy at a given temperature and ν defined as:

$$\frac{\langle E\rangle - E_{eq}(T)}{\sigma} = \nu. \qquad \text{(eq. 2)}$$

A crucial idea that was generated by the work is to keep the system out of equilibrium. This idea is in agreement with the schedule produced in this work. The system should not be allowed to reach equilibrium. When equilibrium occurs the temperature is no longer driving the system towards a new state and the system stagnates in making progress towards assembly.

The form of the schedule produced by the Constant Thermodynamic Speed Model is dependent of the heat capacity and the relaxation time. If ε and C are assumed to be constants, the annealing schedule yielded is an exponential decay function. While if C is assumed to be proportional to T^{-2} and ε is proportional to exp(a/T) where a is some

constant, the form of the schedule gotten is in agreement with the results presented in this work. However, the constants needed to complete this form are not predicted by the Constant Thermodynamic Speed Model. Furthermore the assumptions about the dependence of the temperature and relaxation time are not justified.

The heat capacity model is another approach to this problem. The key assumption made by this model is that the time rate of change of the entropy should remain constant. With some manipulation the following schedule is created:

$$\frac{\Delta T}{\Delta t} = \lambda T C^{-1}, \qquad \text{(eq. 3)}$$

with λ = the constant time rate of change of entropy.

The assumption regarding the time rate of change of the entropy has an important but not obvious implication. This assumption calls for more time to be spent in a temperature range that corresponds to a strong change in entropy. The times when a system has a dramatic change in entropy is when a phase change occurs, gas to liquid, liquid to solid etc. The idea of giving more time in a temperature range that corresponds to a dramatic system change is sound but not optimal.

Numerical Methods and System:

The system experimentally explored was translated into a potential to represent a simplified version of what the physics dictating the behavior of the actual experiment. The potential is piecewise in nature and is a Coulombic term to represent the electrostatic forces in play as well as a repulsive term to not allow the spheres from overlapping since such behavior is unphysical. The potential is defined as such:

$$U(r) = \frac{q_1 q_2}{\varepsilon_0 r} + C(r_{overlap})\text{^}3, \qquad \text{(eq.4)}$$

with r= the distance between the center of two spheres, q = the charge of the sphere, ε_0 = the dielectric constant = 1, $r_{overlap}$ = max[$2r_0$-r,0] and C = 1000. The system also assumes the mass of all spheres to be 1 and the radius of all spheres, r_0, to be 1 as well.

It must be noted that the limit of the potential as the distance between the two oppositely charged particles goes to zero is negative infinity. This is also unphysical but unimportant as the system did not have enough kinetic energy to go over the barrier needed to reach the infinite well. It is also important to note that this is a conservative system in regards to energy. This aspect is not similar to the physical system which is susceptible to energy loss through the friction and inelastic collisions with other particles and the system's boundaries. Since the system is conservative all collisions between particles and the systems surroundings are elastic. The system is assumed to be surrounded by a box as it was in the physical experiment. When a particle integrated into the box its position and velocity vector was reflected around the axis of the boundary. Another aspect of the physical system not included in the model is the angular momentum or rolling experienced by the particles. The angular momentum imparted on the particles may affect their trajectories and thus the way in which they arrange, however angular momentum is probably not a significant effect. Furthermore such complications are outside the goals of the work and would be unnecessary complications.

The technique to predict the motion of a system of particles is an algorithm known as the velocity-Verlet algorithm. Given a set of initial positions and velocities the

algorithm can integrate through time, or move forward through time, and predict the way the system will move based on the potential energy function which describes the system. The way the algorithm works is by first calculating the forces on each particle then applying that force onto the particle for a short period of time as if the force was constant. Based on this force vector, the mass of the particle, the particles previous velocity and position, the particle position is updated along with its velocity based on elementary physics. This is all based around the assumption that the force is constant for a brief instant. An important aspect of this algorithm, which is essentially a numerical differential equation solver, is that it conserves energy over time. This property makes the algorithm ideal for running dynamics on conservative systems.

The algorithm will temporarily not conserve energy when two particles collide or more generally when the system is integrated into a region of the potential that is too high in energy. As the algorithm works it will occasionally update the position of a particle into a high potential energy position, an area that it could physically never reach, such as two particles overlapping. What happens next is that the system will be expelled from this region of high energy with high kinetic energy. As long as the algorithm does not place the system too high into the normally forbidden region the system will quickly lose its excess energy and re-stabilize at the correct energetic level. However, if the time step used is too large it will integrate into a region of with such high potential that the system cannot handle the excess amount of energy and energy is no longer conserved. When energy is no longer conserved and the trajectory predicted by the algorithm should no longer be considered valid.

To fix such a problem the time step can be shortened. The time step is the only adjustable parameter in the algorithm. The time step can be considered the amount of time that the potential is assumed to be constant. In an actual system the potential felt is continuously changing as the positions of the particles change. A shorter time step will be more physically accurate and prevent the system from going into high potential energy regions. The draw back of shortening the time step is that more calculations must be done to predict trajectories of equal time. So the longest time step that will conserve energy should be used to conserve computing resources. The ideal time step can be found by experimenting with the parameter, running dynamics and keeping track of the total energy.

In order to justify an assumption made in the schedule development the energetic barrier between two states needed to be calculated. This calculation is done using the climbing-image Nudged Elastic Band (NEB) method. This algorithm takes a final and initial state, which are both local minimums, and finds the minimum energy path (MEP) between the two states. The highest point on this path is known as the transition state (TS) and the energy difference between the TS and the first minimum is the activation energy or energy barrier for the process. The magnitude of the activation barrier is crucial in predicting the rate at which a process or chemical reaction will take place. The higher a barrier the slower the rate will be as compared to a low activation barrier.

The NEB method works by making a linear interpolation between the final and initial state. Physically this can be thought of as the algorithm guessing that the reaction proceeded in a linear fashion, with the atoms that changed position doing so in a straight line. The algorithm uses a certain amount of points along this path, these are called

images. These images are best considered as points on a high dimensional potential energy surface. These points are connected by a spring constant in this potential energy surface and the whole system of images is allowed to relax with the initial and final states acting like anchors. To improve the effectiveness of the algorithm only the parallel portion of the spring force and the perpendicular component of the force due to the potential surface are considered. Perpendicular and parallel are relative to a smooth high-dimensional curve passing through the images. To find the saddle point or transition state the image that is at the highest energy climbs up hill. This uphill climbing is done by ignoring the force from the spring and applying the negative force from the potential. This climbing image should find the transition state.

In the experimental system kinetic energy was imparted by oscillating the tray in the lateral axis. This kind of movement is not well defined so the more general and applicable term of temperature was introduced. Temperature is a measure of the average kinetic energy of a system with a well defined probability distribution for the velocity of each particle. To impart a system with a temperature a computational tool called a thermostat was used. There are a variety of thermostats; the two used in this work are an Andersen thermostat and a Nose-Hoover thermostat. The Andersen type thermostat works by changing some or all of the velocities of the atoms or particles in the system to the correct distribution for the given temperature. This reassigning of velocities happens with some probability after each time step with a small probability chosen such that expectation value of the time between velocity reassignments is a set parameter. Other parameters for the Andersen type thermostat are the amount of the systems original velocity is kept and what portion of the system is susceptible to having its velocities

reassigned. The Nose-Hoover thermostat works by coupling the system to extra degrees of freedom, these degrees of freedom are kept at constant energy. The coupling between the system and the extra degrees of freedom occurs at a specific frequency, the problem is that if the frequencies do not agree they do not couple well and little energy is transferred. To avoid this problem several coupling frequencies are used in the hope that at least one of those frequencies will couple well to the actual system. A problem with all thermostats is that it disrupts the dynamics of the system, however this is inevitable and it is generally better to sample a set of systems with the correct distribution of kinetic energy than worry about the exact trajectory.

In the course of the work numerical minimum finders were used. Ideally a system can have its local minimums found by taking the gradient of the potential defining the system setting it equal to zero and solving for the appropriate positions. This is only possible is trivial systems, thus it is necessary to numerically find local minimums. There are several techniques for approximating this value. Perhaps one of the simplest methods and one employed in the work is the steepest decent method. The minimum is found by following the steepest negative gradient, i.e. you move downhill in the steepest direction. This technique is analogous to letting a ball role freely to find the bottom of the pit. The point will be reevaluated at discrete intervals and the direction is allowed to change as the curvature changes, eventually the point will reach the bottom and will stop searching when its energy stops decreasing within some cut off criterion.

Annealing Schedule Development and Discussion

Intrinsic Energy:

In order to optimize self-assembly a metric of self-assembly must first be determined. From the definition of self-assembly, a system becoming more order, a term such as entropy would lend itself to measuring this phenomenon. Unfortunately such a term is difficult to calculate directly and thus unpractical for measuring self-assembly. Due to the fact that the system in its most ordered form, a perfect square if geometrically allowed, has the lowest potential energy of all configuration with that amount of spheres, a potential energy term is viable candidate for measuring the systems self-assembly. Fortunately calculating the potential energy directly is easy with a well defined potential. However, a dynamic system such as the one in question does not have a stable amount of potential energy. This is because energy is transferred between potential and kinetic energy as the system integrates through time. As a time average the amount of kinetic and potential energy is a smooth function but in the short term the measurement of equilibrium potential energy as a function of time is not smooth and rather noisy. To avoid this problem a new term was introduced; the intrinsic energy or $\bar{U}$. This term is calculated by taking a system of interest and first setting all of the particles velocities to zero, quenching the system and removing all of the kinetic energy. This alone would not fix the problem of having a noisy potential energy value; however, the system is then relaxed to its local minimum. The local minimum was found numerically with a steepest dissent type method. An advantage to $\bar{U}$ is that systems of high disorder, which are essentially in the gas phase, have nearly the same $\bar{U}$ as long as the system is in the gas

phase. This property of considering all gases to have the similar amount of order is similar to entropy.

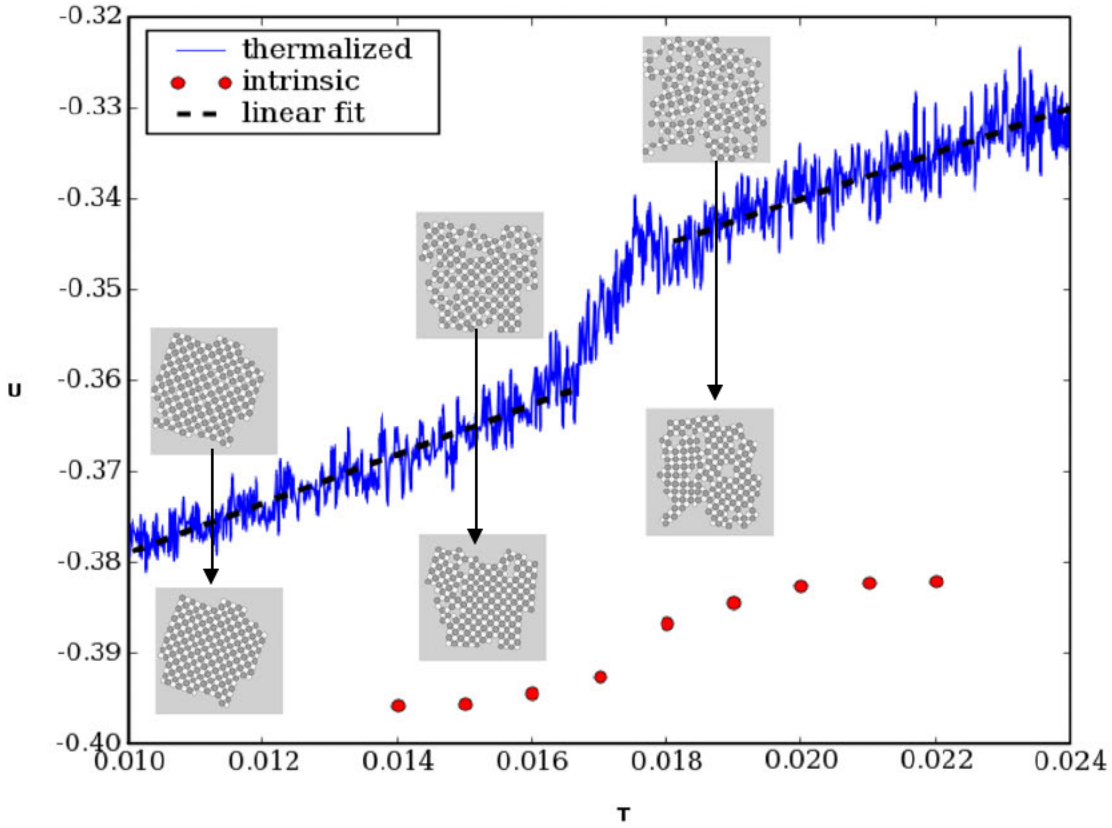

Figure 1. The arrows between the images represent the minimization process of the top system to the bottom system. The systems presented here consisted of 400 particles.

Underlying Schedule Assumptions:

An assumption about the rate at which the system will reach its equilibrium intrinsic energy was made. The formulation of this rate is:

$$\frac{d(\overline{U} - \overline{U}_0)}{dt} = (\overline{U} - \overline{U}_0)\nu \exp\left(\frac{-\Delta E}{kT}\right). \qquad \text{(eq. 5)}$$

The $\bar{U}_0$ term is the systems equilibrium intrinsic energy at a given temperature. This value is calculated over an average of systems allowed to reach equilibrium at that temperature. The term ν can be considered a rate term with units of inverse time. The rate that is being described by ν is the rate at which the system will try to rearrange itself to a more ordered configuration. The exponential term can be viewed as a probability of the move to a new arrangement being successful. The ΔE term is the activation barrier term for process that governs self-assembly. The larger the ΔE term is for a process the harder it is for that process to take place. The kT term can be thought of the amount of thermal or kinetic energy in the system where T is the temperature and k is the Boltzmann constant. The Boltzmann constant can be considered a term to fix the failure of temperature to assign a distribution of kinetic energies with the appropriate scale and units. The kT term can also be considered as how hard a system is trying to overcome its barriers. The higher the temperature the higher the kinetic energy the more chance it has of escaping over a barrier. Hence, as kT increases the probability of the system overcoming the barrier to self-assembly becomes more probable. The set of terms are from a common rate equation for chemical reactions known as the Arrhenius equation. The proportionality term U_0-U states that the further the system is away from its equilibrium intrinsic energy the faster it will return to its equilibrium value. This can be justified by considering a system with some number of defects which causes it to have an intrinsic energy higher than its equilibrium intrinsic energy. The more defects a system has the more likely that a defect gets annealed over a certain period of time. Thus its return to equilibrium will be faster the further away from equilibrium it is and will slow down as more defects are annealed and the system reaches equilibrium.

Assumption Justification:

Implicit in equation 5 is the assumption that the process of self-assembly is governed by one barrier, ΔE. The physical interpretation of the single value for ΔE is that only one process is responsible for self-assembly. The physics of self-assembly are more complicated than the assumption of one ΔE would imply. The process of self-assembly is not governed by one process alone. Instead, the use of one ΔE should be viewed as a simplifying assumption. Because using one barrier energy is a simplifying assumption, the validity of this assumption must be evaluated. Since the model being used is of the Arrhenius form the value of ΔE can be determined by an Arrhenius plot. An Arrhenius plot is the graph of the natural log of the rate in question versus the inverse of temperature. If a process is controlled by on value for the activation barrier then the Arrhenius plot should be linear with the slope of this line giving the magnitude of the activation barrier. For self-assembly an Arrhenius plot yielded a linear range at temperatures at and below the melting point. The linearity of this line was not perfect, see figure 2. The slope had a relative error of over 10 percent.

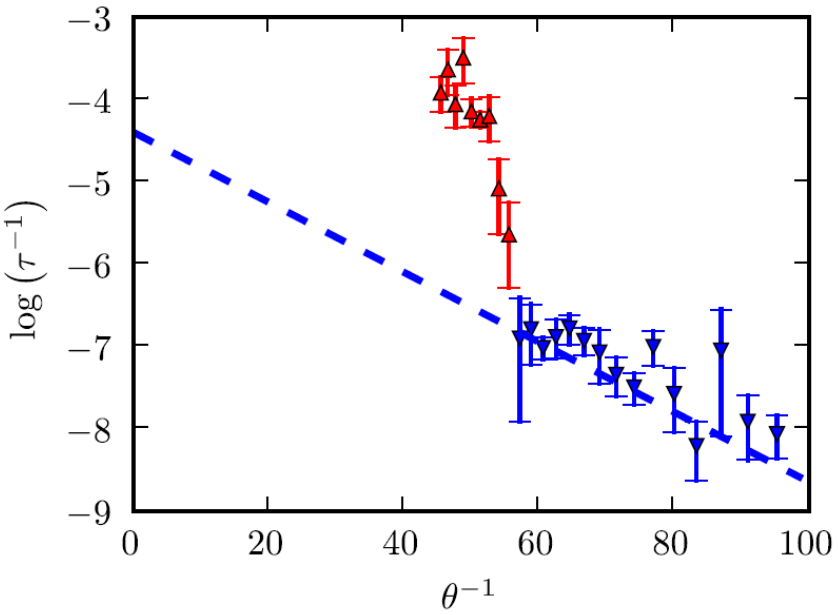

Figure 2. This is the Arrhenius plot for self-assembly. The θ^{-1} term should be considered T^{-1} and the τ^{-1} term should be considered rate. The blue triangles are data points in the cold, below the phase transition temperature and the red data points are above the phase transition. The blue dashed line is the best fit line for the blue data points.

It should be noted that the temperature range above the phase transition temperature was excluded for the linear fit of the Arrhenius plot. The disregarding of the high temperature data can be justified by considering when the self-assembly process occurs. At temperatures above the phase change temperature the system behaves like a gas. In this regime no crystals can be formed so no assembly will occur. The assembly process begins once the system is cool enough to start forming crystals; because of this all mechanisms that will control for self-assembly must be considered at and below the phase change temperature. The phase change temperature is at .018kT.

Within in the context of the one activation barrier assumption being correct it was set upon to find a process which matched the barrier energy of the Arrhenius plot and seemed to be a reasonable mechanism for self-assembly. Several rearrangements were considered but the most reasonable one found was a surface diffusion mechanism. The

mechanism involved a pair of oppositely charged spheres hopping over one another on the surface of a crystal (see figure number). The barrier energy for this reaction was .05 energy units; this is in reasonable agreement with the prediction made by the Arrhenius plot which gave a barrier height of .043 ± .06 energy units.

The energy units used are unique to the system and it is not useful to convert them into common units. The import aspect of the energy units used is for comparison purposes. To give a sense of the system it should be remembered that the energy of a sphere in a lattice is .8 energy units and the energy of a surface sphere is .6 energy units.

Another mechanism considered to explain self-assembly was the surface replacement mechanism (see figure 3). The barrier energy of this mechanism was a function of the lattice size. The larger the lattice the higher the barrier energy for the mechanism became. This can be rationalized be considering that at the transition state all spheres on the surface of interest become displaced. The larger the surface the more spheres become displaced the more the system energy increases. Because this process was such a strong function of system size it was not a good candidate for explaining the single value for ΔE. Furthermore the limit for large systems became higher than the predicted value.

Another rejected mechanism considered as a candidate for governing self-assembly was the surface diffusion of one sphere. The issue with this mechanism is it involved a single unpaired sphere; such an occurrence is rare in our model system. The rarity of an unpaired sphere is due to the energetic benefit of finding an oppositely charged sphere and the lack of a barrier for this process to occur. Furthermore it was

discovered that a single atom does not diffuse across the surface of a crystal but rather must dissociate from the surface of the crystal and reattach in a new position.

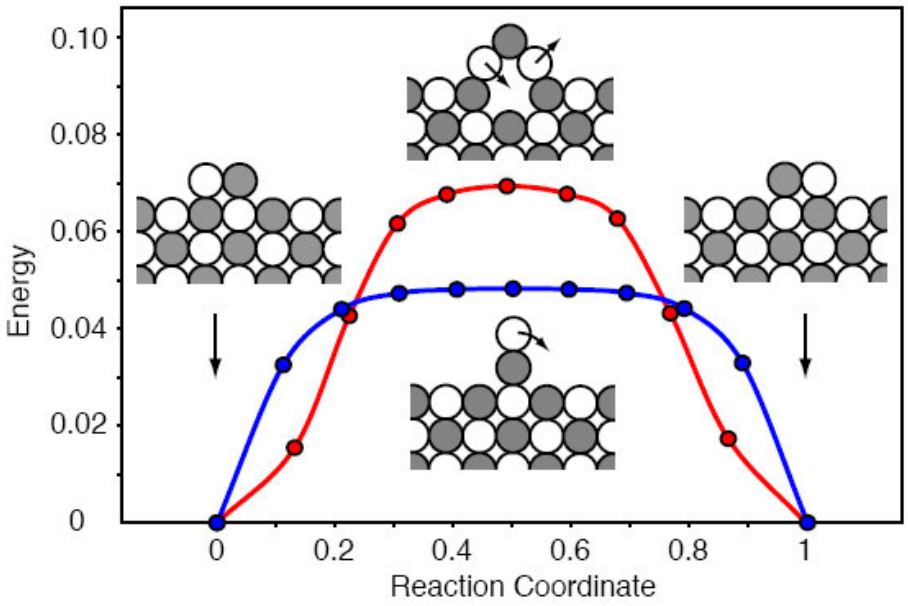

Figure 3. The bottom image shows the transition state for the surface hopping mechanism represented with the blue line. The top image shows the transition state of the surface replacement mechanism at the limit of an infinitely long surface represented in red.

Mechanisms considered for self-assembly that involved internal rearrangements were ruled out as the governing mechanism due to the high energies involved in these transitions. Other mechanisms were found to be lower in energy than predicted by the Arrhenius plot and thus eliminated as rearrangement mechanisms. The annealing of a single site defect by a single sphere occurs with a low barrier on the order of .001 while a sphere changing spots on a defective corner site is .023 energy units. A variety of these processes and the associated energies can be found in the appendix.

The process of self-assembly is inherently complicated and should not be considered to be governed by one process. The results of the Arrhenius plot should be interpreted as an ensemble of process with one process the dominate factor. This can be

justified by considering the uncertainty in linear fit of the Arrhenius plot, the disagreement between the Arrhenius plot energy and the complex nature of self-assembly.

The surface hopping mechanism is between two states of equivalent energy. By the metric used to measure assembly, it in no way helps the system assemble. Instead this process can be thought of the most efficient way spheres can move about the surface of a crystal to find defect sites. Once a defect site is found by the hopping pair it can fill in a vacant site in either a spontaneous manner or with a barrier energy much lower than the surface diffusion mechanism. Hence, the surface diffusion should be considered the rate limiting step for annealing.

Schedule Creation:

In order to apply control theory to create a schedule the equilibrium intrinsic energy as a function of temperature needed to be determined. Data points were produced computationally by allowing the system time to reach equilibrium and then calculating the intrinsic energy. Based on these data points a best fit function was created in the temperature regime below the melting point. The function used was exponential was of the form:

$$V(T) = \overline{U}_S + \gamma \exp\left[-\beta\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \qquad \text{(eq. 6)}$$

The terms β, γ, T_m and $\bar{U}_S$ are fitting parameters with T_m being considered the melting temperature. Other than yielding a good fit the form of the function can be justified by considering the $\bar{U}_S$ term as the energy of the perfect crystal and exponential term as the probability of a defect at a given temperature multiplied by the energetic penalty associated with the defect. The term V is the systems equilibrium intrinsic energy for a given temperature.

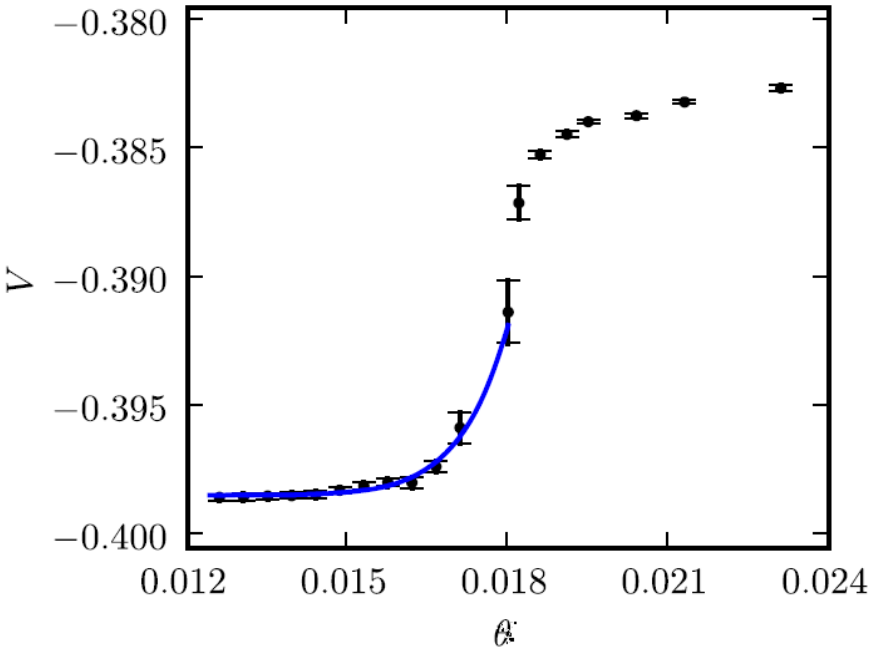

Figure 4. The term V should be considered equilibrium intrinsic energy and the term θ should be considered temperature. The black dots represent computationally created data while the blue line is the best fit line form equation 6.

Classical control theory yields the optimal relationship between $\bar{U}$ and T to be:

$$\overline{U} = \overline{U}_S + \frac{(\Delta E + \beta)\gamma}{\alpha} \exp\left[-\beta\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \quad \text{(eq. 7)}$$

This relationship in addition to equation 5 yields of differential equation for temperature that yields the optimal schedule:

$$T(t) = \left(\frac{\Delta E}{\log[\exp(\Delta E / T_0) + \Delta E \nu t / (\Delta E + \beta)]} \right). \qquad \text{(eq. 8)}$$

The value of the initial temperature T_0 is given by:

$$\frac{1}{T_0} = \frac{1}{T_m} - \frac{1}{\beta} \log\left(\frac{\Delta E(\overline{U}_0 - \overline{U}_S)}{(\Delta E + \beta)\gamma} \right), \qquad \text{(eq. 9)}$$

with the value $\bar{U}_0$ being a prescribed value for the intrinsic energy at the start of the schedule.

Results

The results of the schedule are best summarized in figure (5).

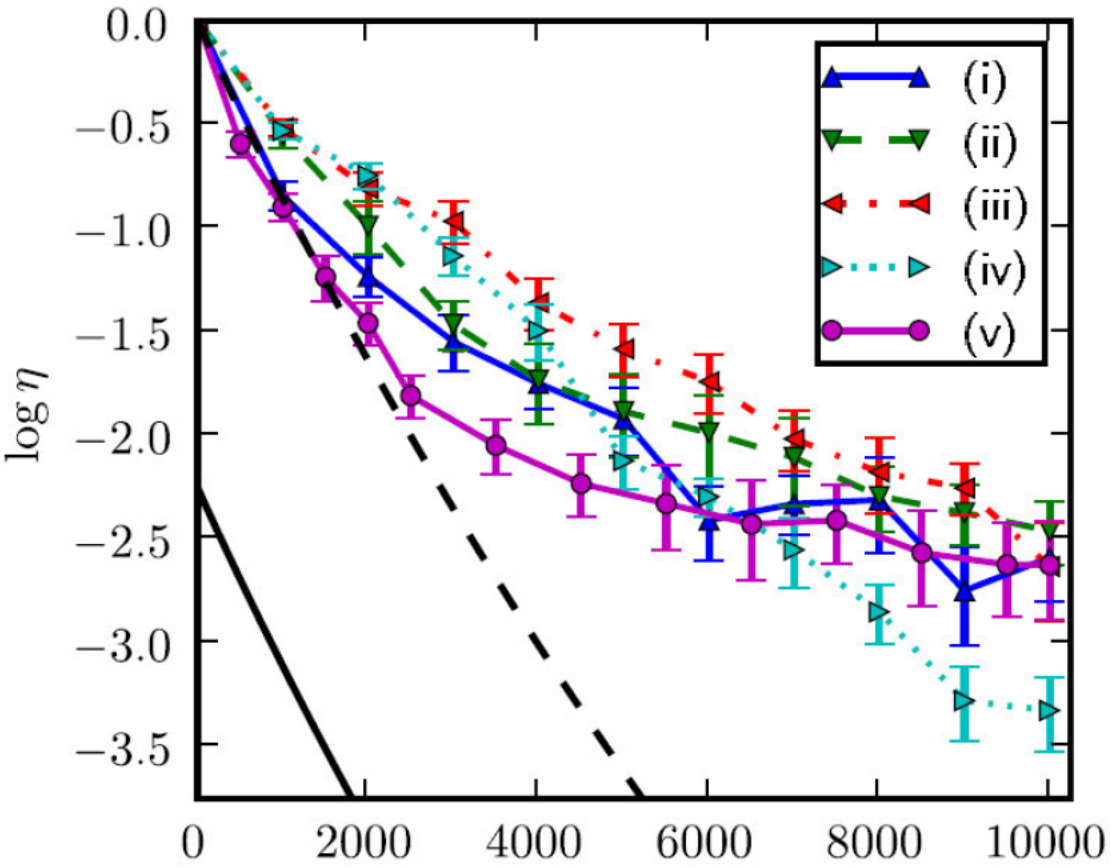

Figure 5. The figure represents the results of running various schedules. Schedule (i) is held at constant temperature, (ii) is a constant change in temperature, (iii) is the constant energy rate schedule (eq. 3), (iv) is the constant thermodynamic speed schedule (eq. 2) and (v) is the optimal schedule (eq. 8). The dashed black line is the idealized performance of the optimal schedule and the solid black line is the reference of V(T(t)) from equations 6 and 7.

The term used to evaluate the schedules, η is defined as:

$$\eta = -\frac{\bar{U} - \bar{U}_S}{\bar{U}_G - \bar{U}_S}. \qquad \text{(eq. 10)}$$

Where $\bar{U}$ is the intrinsic energy of the system in question, $\bar{U}_S$ is the intrinsic energy of a perfect square lattice and $\bar{U}_G$ is the equilibrium intrinsic energy of a hot gas. The term η

can be thought of as the distance the system is from the ideal state divided by the maximum distance the system can be from the ideal state.

Discussion of Schedule Results:

The optimal schedule presented here out performs all other schedules for the first 6000 time units. After 6000 time units the constant temperature schedule performs equally well as the optimal schedule and is out performed by the Constant Thermodynamic Speed schedule. The failure of the optimal schedule lies assumption that one activation barrier controls assembly. After a certain level of organization is reached the surface diffusion mechanism is no longer available. At this point the system is locked into a non-optimal, non-square geometry that the surface diffusion mechanism cannot escape from. When this occurs higher barrier for rearrangements must be crossed. Such higher barriers need a higher temperature to be crossed with a reasonably high probability and in a timely manner. Because of this other schedules gain an advantage in providing a higher temperature to allow the system to break out of the higher energy configuration.

Ideally the optimal schedule should perform as well as the reference (black dashed) line in figure 5. The first occurrences of the one barrier assumption breaking down in near 2500 time units when the schedule begins to deviate from the reference line. At this point in the schedule the crystal is in a configuration not readily able to become more organized by mechanisms with barriers similar to that of surface diffusion. The model does not account for such occurrence and losses efficacy relative to the idealized reference at 2500 time units and to other schedules at 6000 time units.

The difficulty in annealing substantially ordered system but are not perfectly ordered is that the temperatures needed to break the system out of its local minimum are relatively substantial. These high temperatures needed have the potential to disorder the system.

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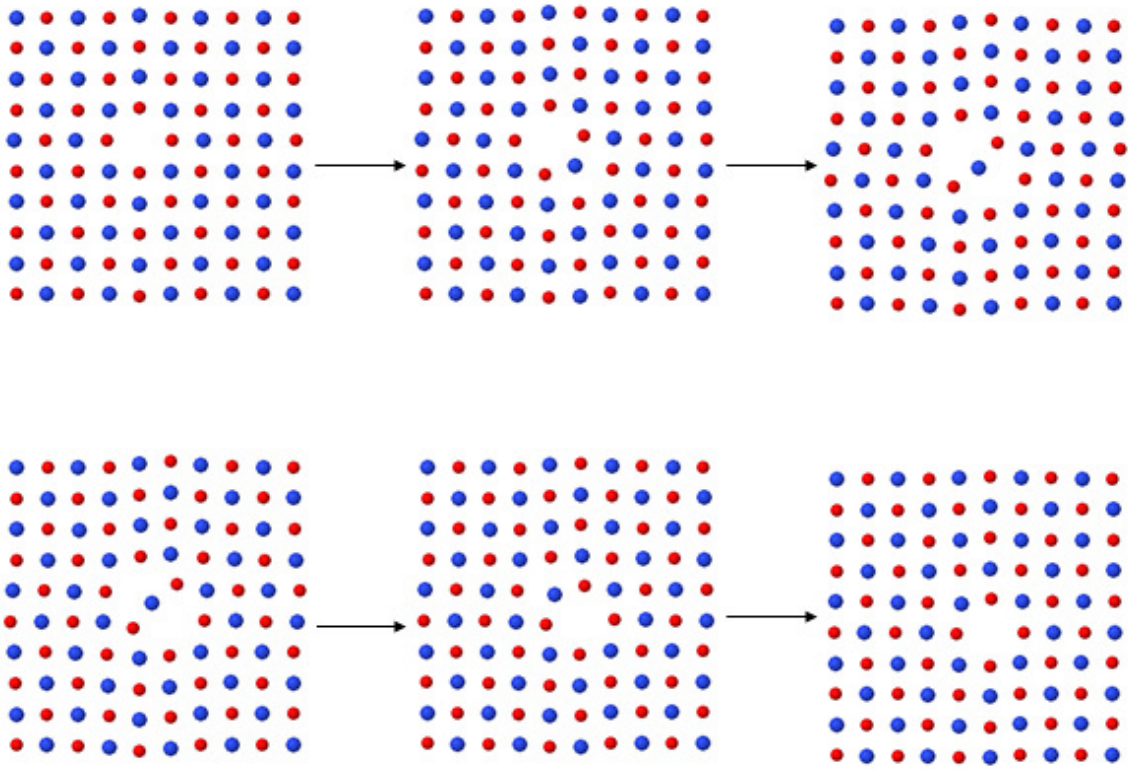
Appendix

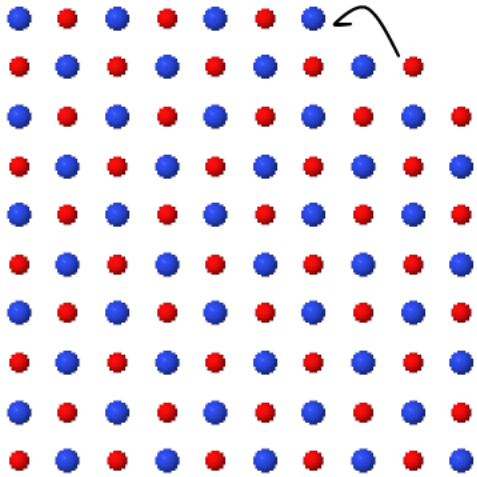
List of Processes and Associated Activation Barriers:

Description:	Energy:
Single Vacancy Diffusion 100 Atom Lattice	0.157
Single Vacancy Diffusion 400 Atom Lattice	0.247
Single Vacancy Diffusion 676 Atom Lattice	0.268
Double Vacancy Diffusion 100 Atom Lattice	0.188
Double Vacancy Diffusion 400 Atom Lattice	0.215
Double Vacancy Diffusion 676 Atom Lattice	0.221

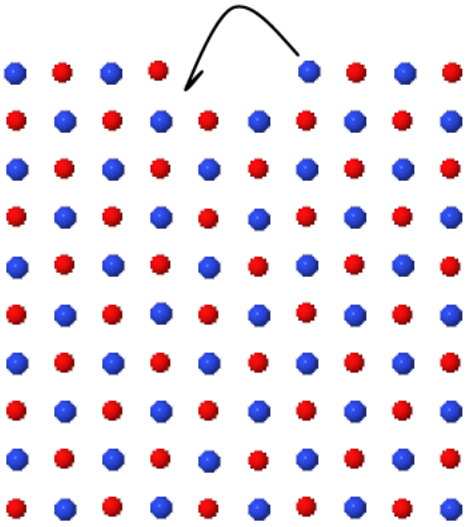
100 Atom Single Vacancy Diffusion



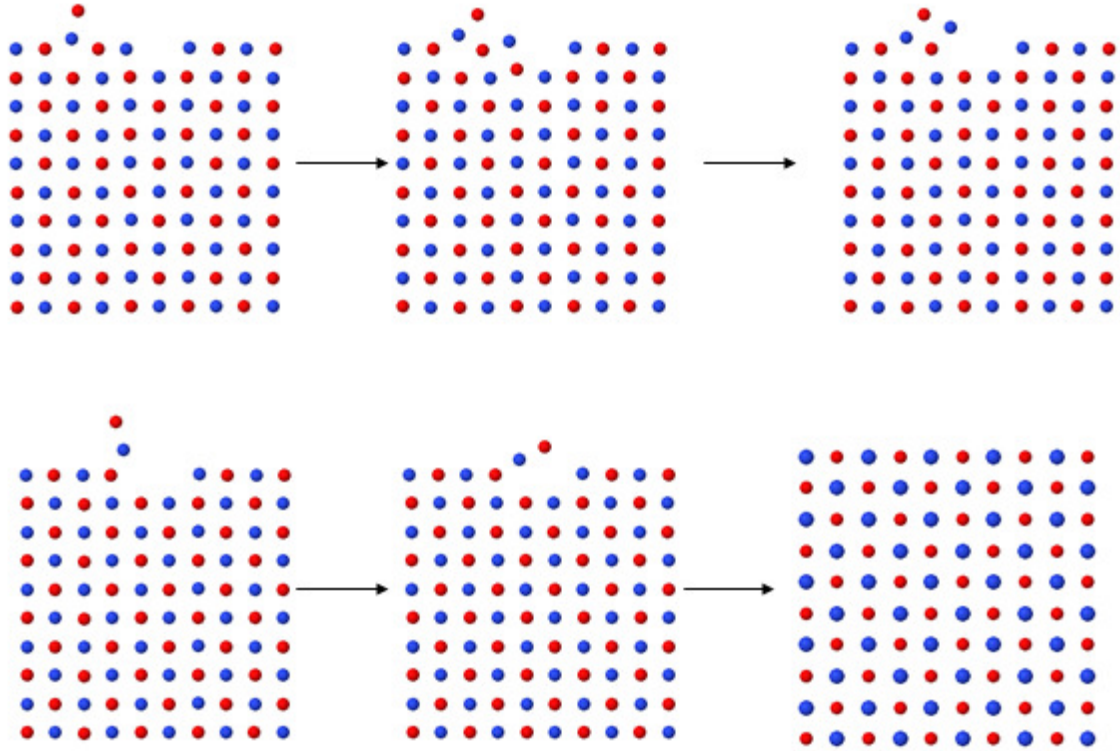
Activation Barrier .023 energy units



Activation Barrier .23 energy units



Activation Barrier .0094 energy units



Activation Barrier .021 energy units